

“On the Relative Importance of SO₂ oxidation to High Dust SCR DeNO_x units”

Morten Thellefsen Nielsen

Haldor Topsøe A/S, Nymoellevej 55, DK-2800 Lyngby, Denmark

E-mail mfn@topsoe.dk, Telephone +45 45 27 23 80, Telefax +45 45 27 29 99

As an undesired side reaction SCR DeNO_x installations oxidize a small amount of the SO₂ in the flue gas, usually less than 1%, but still approximately doubling the SO₃ concentration from the boiler.

Combined with unreacted NH₃ from the SCR or by itself, SO₃ can cause downstream problems such as ammoniumbisulfate (ABS) plugging in air heaters, cold end corrosion and high stack opacity.

In coal fired power plants, the amount and composition of the coal ash can have a major influence on the above mentioned SO₃ effects as especially alkaline components such as CaO, MgO, Na₂O, K₂O and Fe₂O₃ can capture sulfate.

Downstream installations such as ESP and FGD have an influence on the SO₃ emissions. This will be shown in case studies from two U.S. coal fired power plants where SO₃ was measured at the inlet and outlet of the SCR reactor, at the outlet of the ESP, and in the stack.

A correct prediction of the sulfate capture in the fly ash will enable an estimate of the SO₃ concentration downstream the SCR. This knowledge can be used to e.g. optimize the air heater operation, predict the effects of switching coal and the effect of retrofitting the power plant with an SCR DeNO_x unit. Since customers often require the SCR SO₂ oxidation guarantees given under operating conditions, more reliable guarantees can be given with this knowledge.

Based on SO₂ oxidation measurements carried out on European and U.S. power plants and pilot plant experiments, Haldor Topsøe A/S has developed a model that predicts the SO₃ capture in the fly ash at the outlet of the SCR. The model is continually being improved as knowledge is gained from new high dust SCR installations and from the pilot plant.

The pilot plant simulates the flue gas conditions found in high dust SCR's. The experiments are carried out by systematically changing flue gas temperature, residence time, SO₃ concentration and fly ash type and concentration. At each set of conditions the SO₃ capture in the fly ash is determined from measurements of the gas phase SO₃ concentration and analysis of the sulfur content of the fly ash and of the ash collected on the quartz wool filter in the gas sampling probe.

Not surprisingly we have found that the gas phase SO₃ concentration decreases with increasing fly ash concentration. At 350-400 °C (660-750 °F) the residence time seems to be of less importance, which indicates a rather fast SO₃ capture mechanism. At high relative SO₃



concentrations the availability of alkaline fly ash surface sites limits the capture in the ash. The capture mechanism is modeled by a simple first order dependence on the SO_3 concentration and the number of available alkaline sites.

In addition to the flue gas composition and temperature, the concentration, particle size distribution and the sulfate binding capacity of the fly ash enter into the model to predict the SO_3 capture. The two first properties are usually known but the latter must be measured. Since SO_3 is captured by surface reactions the smallest fly ash particles capture (relatively) most of the SO_3 due to their high specific surface areas and large number concentration. The sulfate binding capacity is measured by saturating the ash with SO_3 . Eventually this enables prediction of the SO_3 capture on basis of an analysis of the coals.

Another very important issue when discussing SO_3 is the determination of the gaseous SO_3 concentration in the flue gas, which by no means is a simple task. The ASTM D-3226-73T standard, the so-called Controlled Condensation method, in which SO_3 is selectively condensed as sulfuric acid, was developed in the early 1960's and is today the most widely used method.

Numerous variants of the Controlled Condensation method exist today, differing in the methods of fly ash filtration, sulfuric acid capture (by condensation) and sulfate determination of the collected sample. The most important differences are related to the fly ash filtration and sulfuric acid capture.

In the course of sampling fly ash builds up on the filter and increases SO_3 capture in the fly ash. On the other hand sufficient gas must be sampled in order to determine the sulfate content in the SO_3 samples with a reasonable accuracy. It is therefore important to minimize the amount of ash deposited on the filter and to change the filter after each measurement to minimize SO_3 capture.

Currently we are testing the influence on SO_3 capture in the fly ash during sampling to get a quantitative description of the effect. Preliminary results clearly show that in the temperature range 300-400 °C (570-750 °F) the ash collected on the filter captures significant amounts of SO_3 during sampling.

The different techniques of SO_3 collection are all based on selective condensation of sulfuric acid on a colder (160-195 °F) surface but not all techniques are suitable for capturing the fine sulfuric acid aerosols, which will form if the gas cooling rate is sufficiently high.

At Haldor Topsøe A/S we use an in-house modification of the ASTM D-3226-73T standard. We have tested our SO_3 measuring equipment in our laboratory and found greater than 99% SO_3 collection efficiency in the condenser.

The conclusion of our investigation is that it is difficult to measure the 'true' gas phase SO_3 concentration in high dust flue gases since the means of ash filtration (and SO_3 collection) can



have a significant effect on the measured SO_3 concentration. There are many pitfalls in the sampling and analysis of SO_3 and it requires both well operating sampling equipment and skilled and experienced operators to get a good result.